J002 Rec'd PCT/PTO 27 MAR 2002

FORM PTO-1390 (REV. 5-93) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER **12093/888**
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371	U S APPLICATION NO. (If known, see 37 CFR 1.5) 10/089270

INTERNATIONAL APPLICATION NO	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/FR00/02680	**28 September 2000 (28.09.2000)**	**30 September 1999 (30.09.1999)**

TITLE OF INVENTION
ZIRCONIUM-BASED ALLOY AND METHOD FOR MAKING A COMPONENT FOR A NUCLEAR FUEL ASSEMBLY WITH SAME

APPLICANT(S) FOR DO/EO/US
Daniel CHARQUET, Jean-Paul MARDON and Jean SENEVAT

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S C 371
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U S.C. 371(f)) immediately rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1)
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau)
   - b. ☒ has been transmitted by the International Bureau.
   - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S C 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   - a ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   - b. ☐ have been transmitted by the International Bureau.
   - c. ☐ have not been made, however, the time limit for making such amendments has NOT expired.
   - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U S C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C 371(c)(4)) (unsigned).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☒ A substitute specification and marked-up version.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information International Search Report and International Preliminary Examination Report

U.S. APPLICATION NO if known, see 37.C.F.R.1.5 10/089270	INTERNATIONAL APPLICATION NO. PCT/FR00/02680	ATTORNEY'S DOCKET NUMBER 12093/888

17. ☒ The following fees are submitted:

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	CALCULATIONS	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EUROPEAN PATENT OFFICE or JPO . . . . . $890 00 International preliminary examination fee paid to USPTO (37 CFR 1.482) . . . $710 00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1 445(a)(2)) . . . . $740 00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . $1,040.00 International preliminary examination fee paid to USPTO (37 CFR 1 482) and all claims satisfied provisions of PCT Article 33(2)-(4) $100.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 890	
Surcharge of $130 00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e))	$	

Claims	Number Filed	Number Extra	Rate		
Total Claims	9 - 20 =	0	X $18 00	$ 0	
Independent Claims	5 - 3 =	2	X $84 00	$168	
Multiple dependent claim(s) (if applicable)			+ $280.00	$ 0	
TOTAL OF ABOVE CALCULATIONS =				$ 1058	
Reduction by ½ for filing by small entity, if applicable Verified Small Entity statement must also be filed. (Note 37 CFR 1 9, 1:27, 1 28)				$ 0	
SUBTOTAL =				$ 1058	
Processing fee of $130.00 for furnishing the English translation later the ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$ 0	
TOTAL NATIONAL FEE =				$ 1058	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40.00 per property +				$	
TOTAL FEES ENCLOSED =				$ 1058	
				Amount to be refunded	$
				charged	$

a. ☐ A check in the amount of $________ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 11-0600 in the amount of **$ 1058.00** to cover the above fees. A duplicate copy of this sheet is enclosed

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0600. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1 494 or 1 495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

John M. Vereb
SIGNATURE

SEND ALL CORRESPONDENCE TO:
Kenyon & Kenyon
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New York, New York 10004

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NAME

CUSTOMER NO. 26646

3/27/02
DATE

[12093/888]

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor(s)	:	Daniel CHARQUET et al.
Serial No.	:	To Be Assigned
Filed	:	Herewith
For	:	ZIRCONIUM-BASED ALLOY AND METHOD FOR MAKING A COMPONENT FOR A NUCLEAR FUEL ASSEMBLY WITH SAME
Examiner	:	To Be Assigned
Art Unit	:	To Be Assigned

Assistant Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT AND
37 C.F.R. § 1.125 SUBSTITUTE SPECIFICATION STATEMENT

S I R:

Kindly amend the above-captioned application before examination, as set forth below.

IN THE SPECIFICATION AND ABSTRACT:

In accordance with 37 C.F.R. § 1.121(b)(3), a Substitute Specification (including the Abstract, but without claims) accompanies this response. It is respectfully requested that the Substitute Specification (including Abstract) be entered to replace the Specification of record.

IN THE CLAIMS:

On the first page of the claims, first line, please add --WHAT IS CLAIMED IS:--.

Please cancel, without prejudice, claims 1 to 9 in the underlying PCT application.

Please add the following new claims:

-- 10. (New) A zirconium based alloy comprising:

zirconium; and

in addition to unavoidable impurities, by weight, from 0.02 to 1% iron; from 0.8 % to 2.3% niobium, less than 2000 ppm tin, less than 2000 ppm oxygen, less than 100 ppm carbon, from 5 to 35 ppm sulphur and from 0.01% to 0.25% in total of at least one of chromium and vanadium, a ratio of a niobium content less 0.5% to an iron content and at least one of not supplemented and supplemented by at least one of a chromium and a vanadium content higher than 2.5.

11. (New) The alloy according to claim 10, wherein the oxygen is from 1000 to 1600 ppm.

12. (New) The alloy according to claim 10, wherein the niobium is from 1 to 1.8 % by weight, the iron is from 0.1 to 0.3% by weight, the tin is from 0.15 to 0.20% by weight, the at least one of chromium and vanadium is from 0.01 to 0.1% by weight, the oxygen is from 1000 to 1600 ppm, the carbon is less than 100 ppm and the sulphur is from 5 to 35 ppm.

13. (New) A tube comprising:

a tubular arranged zirconium-based alloy wherein the alloy comprises:

zirconium; and

in addition to unavoidable impurities, by weight, from 0.02 to 1% iron; from 0.8 % to 2.3% niobium, less than 2000 ppm tin, less than 2000 ppm oxygen, less than 100 ppm carbon, from 5 to 35 ppm sulphur and from 0.01% to 0.25% in total of at least one of chromium and vanadium, a ratio of a niobium content less 0.5% to an iron content and at least one of not supplemented and supplemented by at least one of a chromium and a vanadium content higher than 2.5 in a recrystallized state.

14. (New) A flat product comprising:

an flat arranged zirconium based alloy wherein the alloy comprises:

zirconium; and

in addition to unavoidable impurities, by weight, from 0.02 to 1% iron; from 0.8 % to 2.3% niobium, less than 2000 ppm tin, less than 2000 ppm oxygen, less than 100 ppm carbon, from 5 to 35 ppm sulphur and from 0.01% to 0.25% in total of

at least one of chromium and vanadium, a ratio of a niobium content less 0.5% to an iron content and at least one of not supplemented and supplemented by at least one of a chromium and a vanadium content higher than 2.5 in a recrystallized state.

15. (New) A method of manufacturing nuclear components comprising:

configuring components of a pressurized water reactor from an alloy comprising:

zirconium; and

zirconium; and

in addition to unavoidable impurities, by weight, from 0.02 to 1% iron; from 0.8 % to 2.3% niobium, less than 2000 ppm tin, less than 2000 ppm oxygen, less than 100 ppm carbon, from 5 to 35 ppm sulphur and from 0.01% to 0.25% in total of at least one of chromium and vanadium, a ratio of a niobium content less 0.5% to an iron content and at least one of not supplemented and supplemented by at least one of a chromium and a vanadium content higher than 2.5 in a recrystallized state, wherein water initially contains less than 3.5 ppm of lithium.

16. (New) The alloy according to claim 10, wherein the ratio is higher than 3.

17. (New) The alloy according to claim 10, wherein the iron content does not exceed 0.35%.

18. (New) A method for making a tube to constitute at least one of all and an external portion of at least one of nuclear fuel rod cladding and a guide tube for a nuclear fuel assembly comprising:

producing a bar from a zirconium-based alloy also containing by weight apart from unavoidable impurities, by weight, from 0.02 to 1% iron; from 0.8 % to 2.3% niobium, less than 2000 ppm tin, less than 2000 ppm oxygen, less than 100 ppm carbon, from 5 to 35 ppm sulphur and from 0.01% to 0.25% in total of at least one of chromium and vanadium, a ratio of a niobium content less 0.5% to a iron content and at least one of not supplemented and supplemented by at least one of a chromium and a vanadium content higher than 2.5.;

water-quenching the bar after heating at from 1000°C to 1200°C;

extruding a blank after heating at from 600°C to 800°C;

cold rolling the blank in at least two passes to obtain a tube, with intermediate thermal treatments at from 560°C to 620°C; and

carrying out a final thermal treatment at from 560°C to 620°C, all of the thermal treatments being carried out in at least one of an inert atmosphere and under vacuum.--.

REMARKS

This Preliminary Amendment cancels, without prejudice, claims 1 to 9 in the underlying PCT Application No. PCT/FR00/02680 and those used in the International Preliminary Examination Report. This Preliminary Amendment adds new claims 10 to 18. The new claims, inter alia, conform the claims to U.S. Patent and Trademark Office rules and do not add new matter to the application.

In accordance with 37 C.F.R. § 1.121(b)(3), the Substitute Specification (including the Abstract, but without the claims) contains no new matter. The amendments reflected in the Substitute Specification (including Abstract) are to conform the Specification and Abstract to U.S. Patent and Trademark Office rules or to correct informalities. As required by 37 C.F.R. §§ 1.121(b)(3)(iii) and 1.125(b)(2), a Marked-Up Version of the Substitute Specification comparing the Specification of record and the Substitute Specification also accompanies this Preliminary Amendment. Approval and entry of the Substitute Specification (including Abstract) is respectfully requested.

The underlying PCT Application No. PCT/FR00/02680 includes an International Search Report, dated March 20, 2001, a copy of which is included. The Search Report includes a list of documents that were considered by the Examiner in the underlying PCT application.

The underlying PCT Application No. PCT/FR00/02680 also includes an International Preliminary Examination Report, dated October 11, 2001 and is included herewith.

It is respectfully submitted that the subject matter of the present application is new, non-obvious and useful. Prompt consideration and allowance of the application are respectfully requested.

Respectfully submitted,

KENYON & KENYON

Dated: 3/27/02

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[12093/888]

ZIRCONIUM-BASED ALLOY AND METHOD FOR MAKING A COMPONENT FOR A NUCLEAR FUEL ASSEMBLY WITH SAME

FIELD OF THE INVENTION

The present invention relates to zirconium-based alloys that are to constitute nuclear fuel assembly components usable in light-water nuclear reactors, such as nuclear fuel rod claddings or assembly guide tubes, or even flat products, such as grid plates.

The invention may be used, although not exclusively, in the field of the manufacture of cladding tubes for fuel rods intended for pressurized-water reactors in which the risks of corrosion are particularly high, and also in the field of strip materials used for structural components of the fuel assemblies of such reactors. The invention also proposes a method for making such components.

BACKGROUND INFORMATION

Patent application PCT WO 99/50 854 proposes a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.03 to 0.25% in total of iron, on the one hand, and of at least one of the elements of the group constituted by chromium and vanadium, on the other hand, having from 0.8 to 1.3% of niobium, less than 2000 ppm of tin, from 500 to 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 50 ppm of silicon, the ratio of the iron content, on the one hand, to the chromium or vanadium content, on the other hand, being from 0.5 to 30.

The invention is based on observations made by the inventors in the course of a systematic study of the intermetallic phases and the crystallographic forms of those phases which appear when the relative contents of iron and niobium are varied while the contents of tin, sulphur and oxygen are described in the application mentioned above. It is also based on the observation, made experimentally, that the nature and the crystallographic form of the intermetallic phases containing zirconium, iron

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and niobium have a major influence on corrosion resistance in various environments.

In particular, it has been found that the presence of compounds Zr (Nb, $Fe)_2$ having a crystalline structure with a hexagonal lattice, and of the phase ßNb substantially improves corrosion in the aqueous medium which exists in the majority of pressurized-water reactors.

SUMMARY

The present invention aims especially to provide an alloy which enables components to be obtained wherein the composition may be adapted in an optimum manner to the conditions of use provided for and whose composition is not likely to hamper the manufacturing steps excessively.

To that end, the invention proposes, in particular, a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron having from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and from 0.01% to 0.25% in total of chromium and/or vanadium, the ratio R of the niobium content, less 0.5%, to the iron content, optionally supplemented by the chromium and/or vanadium content, being higher than 2.5. A ratio exceeding 3 may be used. In order to have a particularly high resistance to uniform corrosion, iron content may not exceed 0.35% as an example.

The choice of the ratio R results from the observation that the phase having a hexagonal lattice does not appear until the relation between the content of Fe (and also of Cr and V if they are present) and the content of Nb is such that R exceeds a threshold which depends slightly on the contents of other elements and on the temperature, but is still higher than 2.5.

The oxygen content may be controlled in such a manner that it is from 1000 to 1600 ppm.

The invention also proposes a method for making a tube according to which:

- a bar is produced from a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and from 0.01% to 0.25% in total of chromium and/or vanadium, the ratio of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being higher than 2.5;
- the bar is water-quenched after heating at from 1000°C to 1200°C;
- a blank is extruded after heating at a temperature of from 600°C to 800°C;
- the blank is cold-rolled in at least two passes to obtain a tube, with intermediate thermal treatments at from 560°C to 620°C; and
- a final thermal treatment is carried out at from 560°C to 620°C, all of the thermal treatments being carried out in an inert atmosphere or under vacuum.

The final thermal treatment leaves the tube in the recrystallized state, which promotes creep strength, without modifying the nature of the phases.

With the method described above, the ßNb phase precipitates and the hexagonal-lattice intermetallic compound of the type Zr (Nb, Fe, Cr, V)$_2$ co-exist.

The alloy may also be used to produce flat elements. Those elements are also used in the recrystallized state and can be manufactured by the following sequence: a blank is produced from a zirconium-based alloy also containing, by weight, in addition to unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium and/or vanadium, the ratio of the niobium content less 0.5% to the iron

content, optionally supplemented by the chromium and/or vanadium content, being higher than 2.5,

the blank is cold-rolled in at least three passes, with intermediate thermal treatments and a final thermal treatment,

one of those intermediate thermal treatments or a preliminary thermal treatment before the first cold-rolling pass being effected for a long period of at least 2 hours at a temperature lower than 600°C, and

any thermal treatment following the long treatment and, in particular, the final recrystallization treatment, being effected at a temperature lower than 620°C.

The invention also proposes the application of the above alloy to the production of components of nuclear reactors operating with pressurized water that contains less than 3.5 ppm of lithium.

The existence of the intermetallic compounds, which is due to the presence of iron in a sufficient quantity, and particularly the existence of Zr $(Nb, Fe)_2$, reduces the amount of niobium precipitates in phase ß, but also the niobium content of the solid solution and gives good resistance to uniform corrosion at a temperature of 400°C, which is representative of the temperature that prevails in reactors. For a Fe/Nb ratio lower than 0.25, the ßNb phase is hardly present.

The presence of chromium and/or vanadium as a very partial replacement for iron and/or niobium in the intermetallic precipitates of the type Zr $(Nb, Fe, Cr, V)_2$ has no marked effect on corrosion at 400°C. The improved corrosion resistance at 400°C is maintained especially if the sum Fe+Cr is at least 0.03%.

To summarize, an alloy of the above type having a use in the recrystallized state to increase its resistance to the bi-axial creep of tubes and the aptitude for the pressing of sheet metal has characteristics which are adjustable by regulating the iron/niobium ratio but which are still favorable; in particular, it has a high corrosion

resistance in an aqueous medium at high temperature, the resistance being all the higher if a high iron content is adopted, this being permitted by a high Nb content.

It also has a high creep strength owing to the presence of tin which remains at a very low content and, owing to doping with oxygen, at a content lower than 2000 ppm, which then has no harmful effect on corrosion resistance.

In current reactors, the ranges given below are particularly valuable as a zirconium-based alloy also containing, by weight, apart from unavoidable impurities: from 1 to 1.8% by weight of niobium, from 0.1 to 0.3% by weight of iron, from 0.15 to 0.20% by weight of tin, from 0.01 to 0.1% by weight of chromium and/or vanadium, from 1000 to 1600 ppm of oxygen, less than 100 ppm of carbon and from 5 to 35 ppm of sulphur.

BRIEF DESCRIPTION OF THE DRAWINGS

The above characteristics and others will emerge more clearly on reading the following description of particular embodiments which are given by way of non-limiting example. The description refers to the drawings which accompany it and in which:

Figure 1 is a ternary diagram showing the intermetallic compounds and microstructures which appear for various ranges of composition, in the case of a content of 0.2% of tin, at a temperature of from 560°C to 620°C.

Figure 2 illustrates a fraction of the diagram on a large scale.

DETAILED DESCRIPTION

Referring to the figures, the C, Si and O_2 contents of obtained samples are substantially identical for all of the samples and were lower than the maximum values given above. The tin content was 0.2% and the sulphur content was 10 ppm.

The samples were manufactured by thermo-metallurgical operations at a temperature not exceeding 620°C, any treatment exceeding that value beyond the extrusion operation reducing corrosion resistance at high temperature.

The ternary diagram in Figure 1 shows, for Fe/Nb ratios lower than approximately 0.3, the existence of a region in which the aZr phase (with the exclusion of the bZr phase which is very detrimental from the point of view of corrosion resistance), the bNb phase precipitates and the intermetallic phase Zr $(Nb, Fe)_2$, which has a hexagonal structure, co-exist.

The compounds, corresponding to a ratio (Nb-0.5%)/Fe+Cr+V higher than a threshold which is always higher than 2.5, as an example, are used when the main phenomenon to be combated is uniform corrosion in high-temperature water having a low lithium content.

For a high Fe/Nb ratio, up to a niobium content of the order of 50%, which is higher by more than one order of magnitude than the contents used, the compound $(Zr, Nb)_4Fe_2$, which is face-centered cubic, also appears.

When the conditions of use make it desirable to have intermetallic compounds that have only or predominantly a hexagonal structure, it is found that the result is achieved by adopting a Fe/Nb ratio lower than 0.3, while also respecting the relation (Nb-0.5%)/Fe+Cr+V > 2.5.

A precise study of the diagram for the low Fe and Nb contents shows that the Nb content in solid solution develops with the Fe content, with Nb remaining constant.

As soon as the Fe content exceeds 60-70 ppm for the alloy according to the present invention, the hexagonal Zr $(Nb,Fe)_2$ form appears which substitutes the bNb phase for a ratio by weight of Nb/Fe substantially equal to 2.3.

There then appears the face-centered cubic compound $(Zr, Nb)_4Fe_2$, corresponding to a Nb/Fe ratio substantially equal to 0.6.

This cubic phase $(Zr, Nb)_4Fe_2$ starts to appear for:

1% Nb from 0.29 to 0.44% Fe
1.5% Nb from 0.49 to 0.66% Fe
2% Nb beyond 0.78% Fe

The diagram illustrates that, by simultaneously increasing the content of Nb and of Fe, a higher density of intermetallics is obtained, which promotes corrosion in an aqueous medium.

The following table shows the influence of the increasing iron content, which does not impair uniform corrosion for an alloy with 1% niobium, the other elements having contents such as described above.

Fe % by weight	**Increase in weight in mg/dm^2 415°C vapour, 311 days, 105 bar**
0.03	490
0.15	456
0.29	455

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ABSTRACT

The invention proposes a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron having from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and from 0.01% to 0.25% in total of chromium and/or vanadium, the ratio R of the niobium content, less 0.5%, to the iron content, optionally supplemented by the chromium and/or vanadium content.

ZIRCONIUM-BASED ALLOY AND METHOD FOR MAKING A COMPONENT FOR A NUCLEAR FUEL ASSEMBLY WITH SAME

FIELD OF THE INVENTION

The present invention relates to zirconium-based alloys that are to constitute nuclear fuel assembly components usable in light-water nuclear reactors, such as nuclear fuel rod claddings or assembly guide tubes, or even flat products, such as grid plates.

The invention [has a particularly important]**may be used**, although not [exclusive]**exclusively**,[application] in the field of the manufacture of cladding tubes for fuel rods intended for [pressurised-water]**pressurized-water** reactors in which the risks of corrosion are particularly high, and also in the field of strip materials used for structural components of the fuel assemblies of such reactors. The invention also proposes a method for making such components.

BACKGROUND INFORMATION

Patent application PCT WO 99/50 854 proposes a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.03 to 0.25% in total of iron, on the one hand, and of at least one of the elements of the group constituted by chromium and vanadium, on the other hand, having from 0.8 to 1.3% of niobium, less than 2000 ppm of tin, from 500 to 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 50 ppm of silicon, the ratio of the iron content, on the one hand, to the chromium or vanadium content, on the other hand, being from 0.5 to 30.

The invention is based on observations made by the inventors in the course of a systematic study of the intermetallic phases and the crystallographic forms of those phases which appear when the relative contents of iron and niobium are varied while the contents of tin, sulphur and oxygen are described in the application mentioned

above. It is also based on the observation, made experimentally, that the nature and the crystallographic form of the intermetallic phases containing zirconium, iron and niobium have a major influence on corrosion resistance in various environments.

In particular, it has been found that the presence of compounds Zr (Nb, Fe)$_2$ having a crystalline structure with a hexagonal lattice, and of the phase ßNb substantially improves corrosion in the aqueous medium which exists in the majority of [pressurised-water]**<u>pressurized-water</u>** reactors.[ ]

<u>SUMMARY</u>

The present invention aims especially to provide an alloy which enables components to be obtained [whose]**<u>wherein the</u>** composition [can]**<u>may</u>** be adapted in an optimum manner to the conditions of use provided for and whose composition is not likely to hamper the manufacturing steps excessively.

To that end, the invention proposes, in particular, a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron having from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and from 0.01% to 0.25% in total of chromium and/or vanadium, the ratio R of the niobium content, less 0.5%, to the iron content, optionally supplemented by the chromium and/or vanadium content, being higher than 2.5. A ratio exceeding 3 [is often advantageous]**<u>may be used</u>**. In order to have a particularly high resistance to uniform corrosion, [it is preferable to have an]iron content **<u>may</u>** not [exceeding]**<u>exceed</u>** 0.35%**<u> as an example</u>**.

The choice of the ratio R results from the observation that the phase having a hexagonal lattice does not appear until the relation between the content of Fe (and also of Cr and V if they are present) and the content of Nb is such that R exceeds a

threshold which depends slightly on the contents of other elements and on the temperature, but is still higher than 2.5.

The oxygen content [is advantageously]**may be** controlled in such a manner that it is from 1000 to 1600 ppm.

The invention also proposes a method for making a tube according to which:

- a bar is produced from a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and from 0.01% to 0.25% in total of chromium and/or vanadium, the ratio of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being higher than 2.5;
- the bar is water-quenched after heating at from 1000°C to 1200°C;
- a blank is extruded after heating at a temperature of from 600°C to 800°C;
- the blank is cold-rolled in at least two passes to obtain a tube, with intermediate thermal treatments at from 560°C to 620°C; and
- a final thermal treatment is carried out at from 560°C to 620°C, all of the thermal treatments being carried out in an inert atmosphere or under vacuum.

The final thermal treatment leaves the tube in the [recrystallised]**recrystallized** state, which promotes creep strength, without modifying the nature of the phases.

With the method described above, the ßNb phase precipitates and the hexagonal-lattice intermetallic compound of the type Zr (Nb, Fe, Cr, V)$_2$ co-exist.

The alloy may also be used to produce flat elements. Those elements are also used in the [recrystallised]**recrystallized** state and can be manufactured by the following sequence: a blank is produced from a zirconium-based alloy also containing, by weight, in addition to unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to

2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium and/or vanadium, the ratio of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being higher than 2.5,

the blank is cold-rolled in at least three passes, with intermediate thermal treatments and a final thermal treatment,

one of those intermediate thermal treatments or a preliminary thermal treatment before the first cold-rolling pass being effected for a long period of at least 2 hours at a temperature lower than 600°C, and

any thermal treatment following the long treatment and, in particular, the final [recrystallisation]**recrystallization** treatment, being effected at a temperature lower than 620°C.

The invention also proposes the application of the above alloy to the production of components of nuclear reactors operating with [pressurised]**pressurized** water that contains less than 3.5 ppm of lithium.

The existence of the intermetallic compounds, which is due to the presence of iron in a sufficient quantity, and particularly the existence of Zr $(Nb, Fe)_2$, reduces the amount of niobium precipitates in phase ß, but also the niobium content of the solid solution and gives good resistance to uniform corrosion at a temperature of 400°C, which is representative of the temperature that prevails in reactors. For a Fe/Nb ratio lower than 0.25, the ßNb phase is hardly present.

The presence of chromium and/or vanadium as a very partial replacement for iron and/or niobium in the intermetallic precipitates of the type Zr $(Nb, Fe, Cr, V)_2$ has no marked effect on corrosion at 400°C. The improved corrosion resistance at 400°C is maintained especially if the sum Fe+Cr is at least 0.03%.

To [summarise]**summarize**, an alloy of the above type having a use in the [recrystallised]**recrystallized** state to increase its resistance to the bi-axial creep of tubes and the aptitude for the pressing of sheet metal has characteristics which are adjustable by regulating the iron/niobium ratio but which are still [favourable]**favorable**; in particular, it has a high corrosion resistance in an aqueous medium at high temperature, the resistance being all the higher if a high iron content is adopted, this being permitted by a high Nb content.

[ ]It also has a high creep strength owing to the presence of tin which remains at a very low content and, owing to doping with oxygen, at a content lower than 2000 ppm, which then has no harmful effect on corrosion resistance.

In current reactors, the ranges given below are particularly valuable as a zirconium-based alloy also containing, by weight, apart from unavoidable impurities: from 1 to 1.8% by weight of niobium, from 0.1 to 0.3% by weight of iron, from 0.15 to 0.20% by weight of tin, from 0.01 to 0.1% by weight of chromium and/or vanadium, from 1000 to 1600 ppm of oxygen, less than 100 ppm of carbon and from 5 to 35 ppm of sulphur.

BRIEF DESCRIPTION OF THE DRAWINGS

The above characteristics and others will emerge more clearly on reading the following description of particular embodiments which are given by way of non-limiting example. The description refers to the drawings which accompany it and in which:

[-]Figure 1 is a ternary diagram showing the intermetallic compounds and microstructures which appear for various ranges of composition, in the case of a content of 0.2% of tin, at a temperature of from 560°C to 620°C[;]**.**

[-]Figure 2 [shows]**illustrates** a fraction of the diagram on a large scale.

DETAILED DESCRIPTION

[The]**Referring to the figures, the** C, Si and O_2 contents [were]**of obtained samples are** substantially identical for all of the samples and were lower than the maximum values given above. The tin content was 0.2% and the sulphur content was 10 ppm.

The samples were manufactured by thermo-metallurgical operations at a temperature not exceeding 620°C, any treatment exceeding that value beyond the extrusion operation reducing corrosion resistance at high temperature.

The ternary diagram in Figure 1 shows, for Fe/Nb ratios lower than approximately 0.3, the existence of a region in which the [aZr]**aZr** phase (with the exclusion of the [bZr]**bZr** phase which is very detrimental from the point of view of corrosion resistance), the [bNb]**bNb** phase precipitates and the intermetallic phase Zr (Nb, $Fe)_2$, which has a hexagonal structure, co-exist.

The compounds, corresponding to a ratio (Nb-0.5%)/Fe+Cr+V higher than a threshold which is always higher than 2.5, **as an example,** are used when the main phenomenon to be combated is uniform corrosion in high-temperature water having a low lithium content.

For a high Fe/Nb ratio, up to a niobium content of the order of 50%, which is higher by more than one order of magnitude than the contents used, the compound (Zr, $Nb)_4Fe_2$, which is face-centered cubic, also appears.

When the conditions of use make it desirable to have intermetallic compounds that have only or predominantly a hexagonal structure, it is found that the result is achieved by adopting a Fe/Nb ratio lower than 0.3, while also respecting the relation (Nb-0.5%)/Fe+Cr+V > 2.5.

A precise study of the diagram for the low Fe and Nb contents shows that the Nb content in solid solution develops with the Fe content, with Nb remaining constant.

As soon as the Fe [ ]content exceeds 60-70 ppm for the alloy according to the present invention, the hexagonal Zr $(Nb,Fe)_2$ form appears which substitutes the [bNb]**bNb** phase for a ratio by weight of Nb/Fe substantially equal to 2.3.

There then appears the [face-centred]**face-centered** cubic compound $(Zr, Nb)_4Fe_2$, corresponding to a Nb/Fe ratio substantially equal to 0.6.

This cubic phase $(Zr, Nb)_4Fe_2$ starts to appear for:

1% Nb from 0.29 to 0.44% Fe

1.5% Nb from 0.49 to 0.66% Fe

2% Nb [ ]beyond 0.78% Fe

The diagram [shows]**illustrates** that, by simultaneously increasing the content of Nb and of Fe, a higher density of intermetallics is obtained, which promotes corrosion in an aqueous medium.

The following table shows the influence of the increasing iron content, which does not impair uniform corrosion for an alloy with 1% niobium, the other elements having contents such as described above.

Fe % by weight	Increase in weight in mg/dm^2 415°C vapour, 311 days, [] 105 bar
0.03	490
0.15	456
0.29	455

[12093/888]

ABSTRACT

The invention proposes a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron having from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and from 0.01% to 0.25% in total of chromium and/or vanadium, the ratio R of the niobium content, less 0.5%, to the iron content, optionally supplemented by the chromium and/or vanadium content.

2/PRTS

10/089270

JC15 Rec'd PCT/PTO 27 MAR 2002

ZIRCONIUM-BASED ALLOY AND METHOD FOR MAKING A COMPONENT FOR A NUCLEAR FUEL ASSEMBLY WITH SAME

The present invention relates to zirconium-based alloys that are to constitute nuclear fuel assembly components usable in light-water nuclear reactors, such as nuclear fuel rod claddings or assembly guide tubes, or even flat products, such as grid plates.

The invention has a particularly important, although not exclusive, application in the field of the manufacture of cladding tubes for fuel rods intended for pressurised-water reactors in which the risks of corrosion are particularly high, and also in the field of strip materials used for structural components of the fuel assemblies of such reactors. The invention also proposes a method for making such components.

Patent application PCT WO 99/50 854 proposes a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.03 to 0.25% in total of iron, on the one hand, and of at least one of the elements of the group constituted by chromium and vanadium, on the other hand, having from 0.8 to 1.3% of niobium, less than 2000 ppm of tin, from 500 to 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 50 ppm of silicon, the ratio of the iron content, on the one hand, to the chromium or vanadium content, on the other hand, being from 0.5 to 30.

The invention is based on observations made by the inventors in the course of a systematic study of the intermetallic phases and the crystallographic forms of those phases which appear when the relative contents of iron and niobium are

varied while the contents of tin, sulphur and oxygen are described in the application mentioned above. It is also based on the observation, made experimentally, that the nature and the crystallographic form of the intermetallic phases containing zirconium, iron and niobium have a major influence on corrosion resistance in various environments.

In particular, it has been found that the presence of compounds Zr $(Nb, Fe)_2$ having a crystalline structure with a hexagonal lattice, and of the phase ßNb substantially improves corrosion in the aqueous medium which exists in the majority of pressurised-water reactors.

The present invention aims especially to provide an alloy which enables components to be obtained whose composition can be adapted in an optimum manner to the conditions of use provided for and whose composition is not likely to hamper the manufacturing steps excessively.

To that end, the invention proposes, in particular, a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron having from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and from 0.01% to 0.25% in total of chromium and/or vanadium, the ratio R of the niobium content, less 0.5%, to the iron content, optionally supplemented by the chromium and/or vanadium content, being higher than 2.5. A ratio exceeding 3 is often advantageous. In order to have a particularly high resistance to uniform corrosion, it is preferable to have an iron content not exceeding 0.35%.

The choice of the ratio R results from the observation that the phase having a hexagonal lattice does not appear until the relation between the content of Fe (and also of Cr and V if they are present) and the content of Nb is such that R exceeds a threshold which depends slightly on the contents of other elements and on the temperature, but is still higher than 2.5.

The oxygen content is advantageously controlled in such a manner that it is from 1000 to 1600 ppm.

The invention also proposes a method for making a tube according to which:

- a bar is produced from a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and from 0.01% to 0.25% in total of chromium and/or vanadium, the ratio of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being higher than 2.5;
- the bar is water-quenched after heating at from 1000°C to 1200°C;
- a blank is extruded after heating at a temperature of from 600°C to 800°C;
- the blank is cold-rolled in at least two passes to obtain a tube, with intermediate thermal treatments at from 560°C to 620°C; and
- a final thermal treatment is carried out at from 560°C to 620°C, all of the thermal treatments being carried out in an inert atmosphere or under vacuum.

The final thermal treatment leaves the tube in the recrystallised state, which promotes creep strength, without modifying the nature of the phases.

With the method described above, the ßNb phase precipitates and the hexagonal-lattice intermetallic compound of the type Zr $(Nb, Fe, Cr, V)_2$ co-exist.

The alloy may also be used to produce flat elements. Those elements are also used in the recrystallised state and can be manufactured by the following sequence: a blank is produced from a zirconium-based alloy also containing, by weight, in addition to unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium and/or vanadium, the ratio of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being higher than 2.5,

the blank is cold-rolled in at least three passes, with intermediate thermal treatments and a final thermal treatment,

one of those intermediate thermal treatments or a preliminary thermal treatment before the first cold-rolling pass being effected for a long period of at least 2 hours at a temperature lower than 600°C, and

any thermal treatment following the long treatment and, in particular, the final recrystallisation treatment, being effected at a temperature lower than 620°C.

The invention also proposes the application of the above alloy to the production of components of nuclear reactors

operating with pressurised water that contains less than 3.5 ppm of lithium.

The existence of the intermetallic compounds, which is due to the presence of iron in a sufficient quantity, and particularly the existence of $Zr(Nb, Fe)_2$, reduces the amount of niobium precipitates in phase ß, but also the niobium content of the solid solution and gives good resistance to uniform corrosion at a temperature of 400°C, which is representative of the temperature that prevails in reactors. For a Fe/Nb ratio lower than 0.25, the ßNb phase is hardly present.

The presence of chromium and/or vanadium as a very partial replacement for iron and/or niobium in the intermetallic precipitates of the type $Zr(Nb, Fe, Cr, V)_2$ has no marked effect on corrosion at 400°C. The improved corrosion resistance at 400°C is maintained especially if the sum Fe+Cr is at least 0.03%.

To summarise, an alloy of the above type having a use in the recrystallised state to increase its resistance to the bi-axial creep of tubes and the aptitude for the pressing of sheet metal has characteristics which are adjustable by regulating the iron/niobium ratio but which are still favourable; in particular, it has a high corrosion resistance in an aqueous medium at high temperature, the resistance being all the higher if a high iron content is adopted, this being permitted by a high Nb content.

It also has a high creep strength owing to the presence of tin which remains at a very low content and, owing to doping with oxygen, at a content lower than 2000 ppm, which then has no harmful effect on corrosion resistance.

In current reactors, the ranges given below are particularly valuable as a zirconium-based alloy also containing, by weight, apart from unavoidable impurities: from 1 to 1.8% by weight of niobium, from 0.1 to 0.3% by weight of iron, from 0.15 to 0.20% by weight of tin, from 0.01 to 0.1% by weight of chromium and/or vanadium, from 1000 to 1600 ppm of oxygen, less than 100 ppm of carbon and from 5 to 35 ppm of sulphur.

The above characteristics and others will emerge more clearly on reading the following description of particular embodiments which are given by way of non-limiting example. The description refers to the drawings which accompany it and in which:

- Figure 1 is a ternary diagram showing the intermetallic compounds and microstructures which appear for various ranges of composition, in the case of a content of 0.2% of tin, at a temperature of from 560°C to 620°C;
- Figure 2 shows a fraction of the diagram on a large scale.

The C, Si and O_2 contents were substantially identical for all of the samples and were lower than the maximum values given above. The tin content was 0.2% and the sulphur content was 10 ppm.

The samples were manufactured by thermo-metallurgical operations at a temperature not exceeding 620°C, any treatment exceeding that value beyond the extrusion operation reducing corrosion resistance at high temperature.

The ternary diagram in Figure 1 shows, for Fe/Nb ratios lower than approximately 0.3, the existence of a region in

which the αZr phase (with the exclusion of the βZr phase which is very detrimental from the point of view of corrosion resistance), the βNb phase precipitates and the intermetallic phase Zr $(Nb, Fe)_2$, which has a hexagonal structure, co-exist.

The compounds, corresponding to a ratio (Nb-0.5%)/Fe+Cr+V higher than a threshold which is always higher than 2.5, are used when the main phenomenon to be combated is uniform corrosion in high-temperature water having a low lithium content.

For a high Fe/Nb ratio, up to a niobium content of the order of 50%, which is higher by more than one order of magnitude than the contents used, the compound $(Zr, Nb)_4Fe_2$, which is face-centered cubic, also appears.

When the conditions of use make it desirable to have intermetallic compounds that have only or predominantly a hexagonal structure, it is found that the result is achieved by adopting a Fe/Nb ratio lower than 0.3, while also respecting the relation (Nb-0.5%)/Fe+Cr+V > 2.5.

A precise study of the diagram for the low Fe and Nb contents shows that the Nb content in solid solution develops with the Fe content, with Nb remaining constant.

As soon as the Fe content exceeds 60-70 ppm for the alloy according to the present invention, the hexagonal Zr $(Nb,Fe)_2$ form appears which substitutes the βNb phase for a ratio by weight of Nb/Fe substantially equal to 2.3.

There then appears the face-centred cubic compound $(Zr, Nb)_4Fe_2$, corresponding to a Nb/Fe ratio substantially equal to 0.6.

This cubic phase $(Zr, Nb)_4Fe_2$ starts to appear for:

1% Nb	from 0.29 to 0.44% Fe
1.5% Nb	from 0.49 to 0.66% Fe
2% Nb	beyond 0.78% Fe

The diagram shows that, by simultaneously increasing the content of Nb and of Fe, a higher density of intermetallics is obtained, which promotes corrosion in an aqueous medium.

The following table shows the influence of the increasing iron content, which does not impair uniform corrosion for an alloy with 1% niobium, the other elements having contents such as described above.

Fe % by weight	**Increase in weight in mg/dm^2 415°C vapour, 311 days, 105 bar**
0.03	490
0.15	456
0.29	455

Claims

1. Zirconium-based alloy also containing, by weight, in addition to unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and from 0.01% to 0.25% in total of chromium and/or vanadium, the ratio of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being higher than 2.5.

2. Alloy according to claim 1, containing 1000 - 1600 ppm of oxygen.

3. Alloy according to claim 1, comprising: from 1 to 1.8% by weight of niobium, from 0.1 to 0.3% by weight of iron, from 0.15 to 0.20% by weight of tin, from 0.01 to 0.1% by weight of chromium and/or vanadium, from 1000 to 1600 ppm of oxygen, less than 100 ppm of carbon and from 5 to 35 ppm of sulphur.

4. Cladding tube made from an alloy according to claim 1, 2 or 3, in the recrystallised state.

5. Flat product made from an alloy according to claim 1, 2 or 3, in the recrystallised state.

6. Application of the alloy according to any one of claims 1, 2 and 3 to the production of components of nuclear reactors operating with pressurised water that initially contains less than 3.5 ppm of lithium.

7. Alloy according to claim 1, characterised in that said ratio is higher than 3.

8. Alloy according to claim 1, characterised in that the iron content does not exceed 0.35%.

9. Method for making tubes that are to constitute all or the external portion of a nuclear fuel rod cladding or a guide tube for a nuclear fuel assembly, characterised in that:

a bar is produced from a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and from 0.01 to 0.25% in total of chromium and/or vanadium, the ratio of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being higher than 2.5;

the bar is water-quenched after heating at from 1000°C to 1200°C;

a blank is extruded after heating at from 600°C to 800°C;

the blank is cold-rolled in at least two passes to obtain a tube, with intermediate thermal treatments at from 560°C to 620°C; and

a final thermal treatment is carried out at from 560°C to 620°C, all of the thermal treatments being carried out in an inert atmosphere or under vacuum.

(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATION EN MATIÈRE DE BREVETS (PCT)

(19) Organisation Mondiale de la Propriété Intellectuelle
Bureau international

(43) Date de la publication internationale
5 avril 2001 (05.04.2001)

PCT

(10) Numéro de publication internationale
WO 01/24194 A1

(51) Classification internationale des brevets[7]: G21C 3/07, C22F 1/18, C22C 16/00

(21) Numéro de la demande internationale: PCT/FR00/02680

(22) Date de dépôt international: 28 septembre 2000 (28.09.2000)

(25) Langue de dépôt: français

(26) Langue de publication: français

(30) Données relatives à la priorité:
99/12248 30 septembre 1999 (30.09.1999) FR

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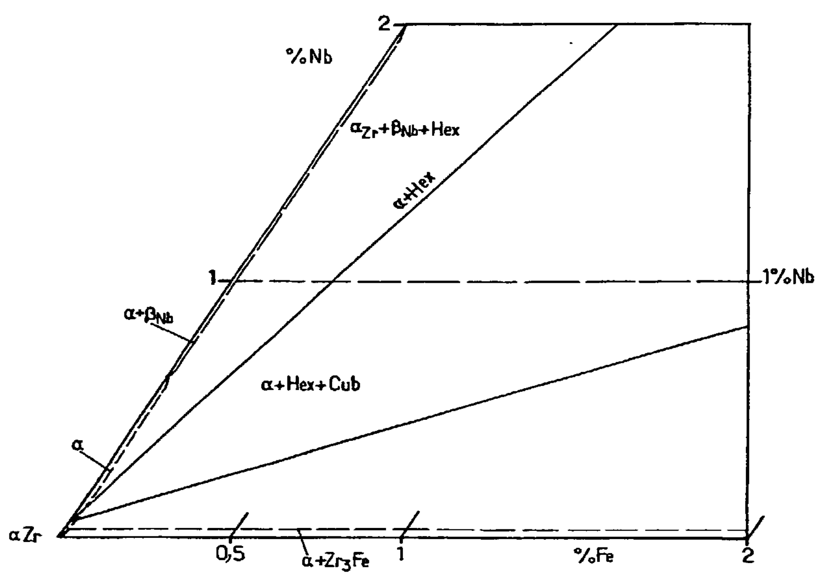
(84) États désignés *(régional)*: brevet européen (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

[Suite sur la page suivante]

(54) Title: ZIRCONIUM-BASED ALLOY AND METHOD FOR MAKING A COMPONENT FOR A NUCLEAR FUEL ASSEMBLY WITH SAME

(54) Titre: ALLIAGE A BASE DE ZIRCONIUM ET PROCEDE DE FABRICATION DE COMPOSANT POUR ASSEMBLAGE DE COMBUSTIBLE NUCLEAIRE EN UN TEL ALLIAGE



(57) Abstract: The invention concerns a zirconium alloy for nuclear reactor components, containing, besides the unavoidable impurities, 0.02 to 1 % iron, 0.8 to 2.3 % niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than a total of 0.25 % of chromium and/or vanadium. The ratio of niobium content at less than 5 % over the iron content, optionally completed with chromium and/or vanadium content, is more than 2.5.

[Suite sur la page suivante]

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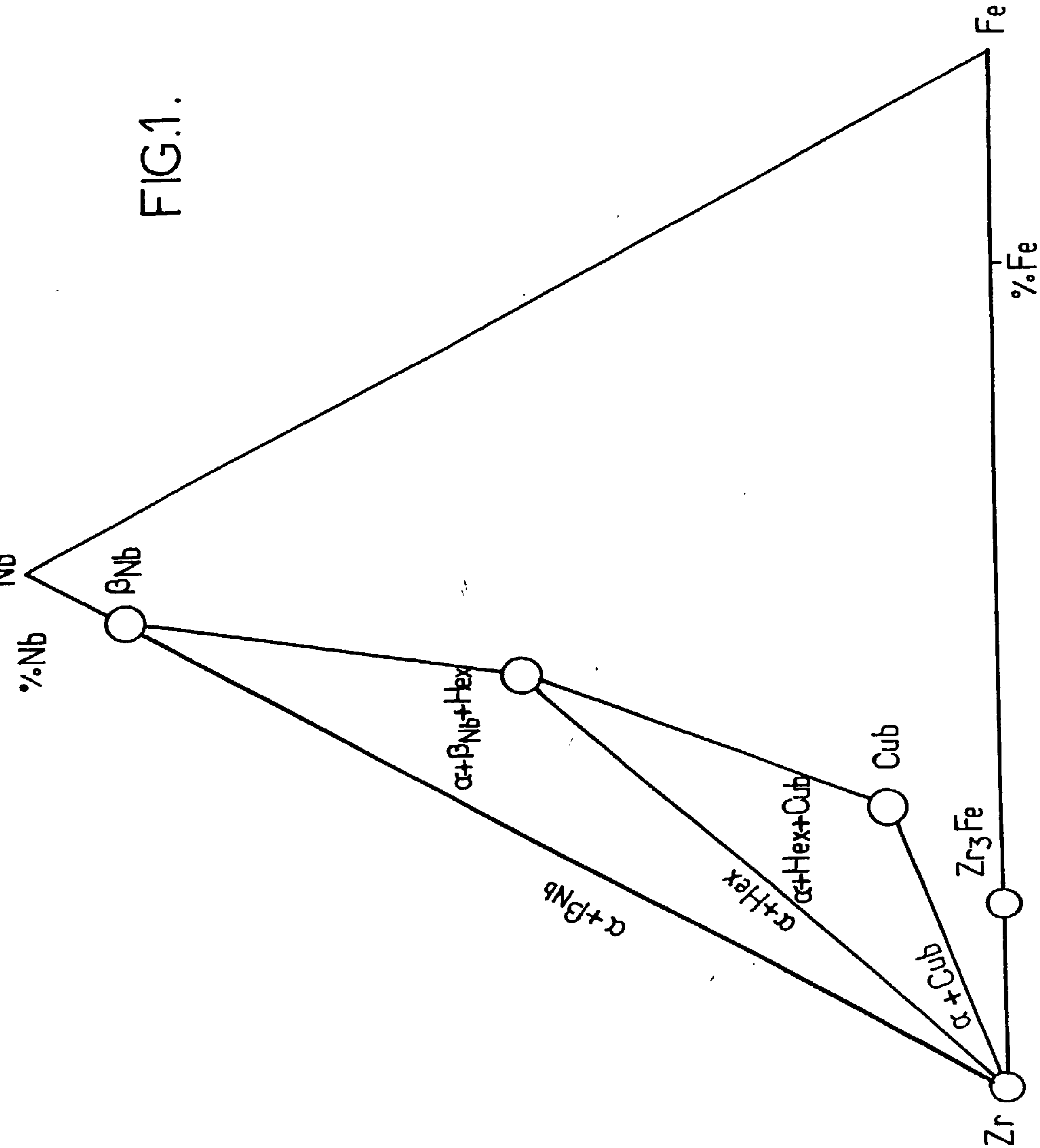
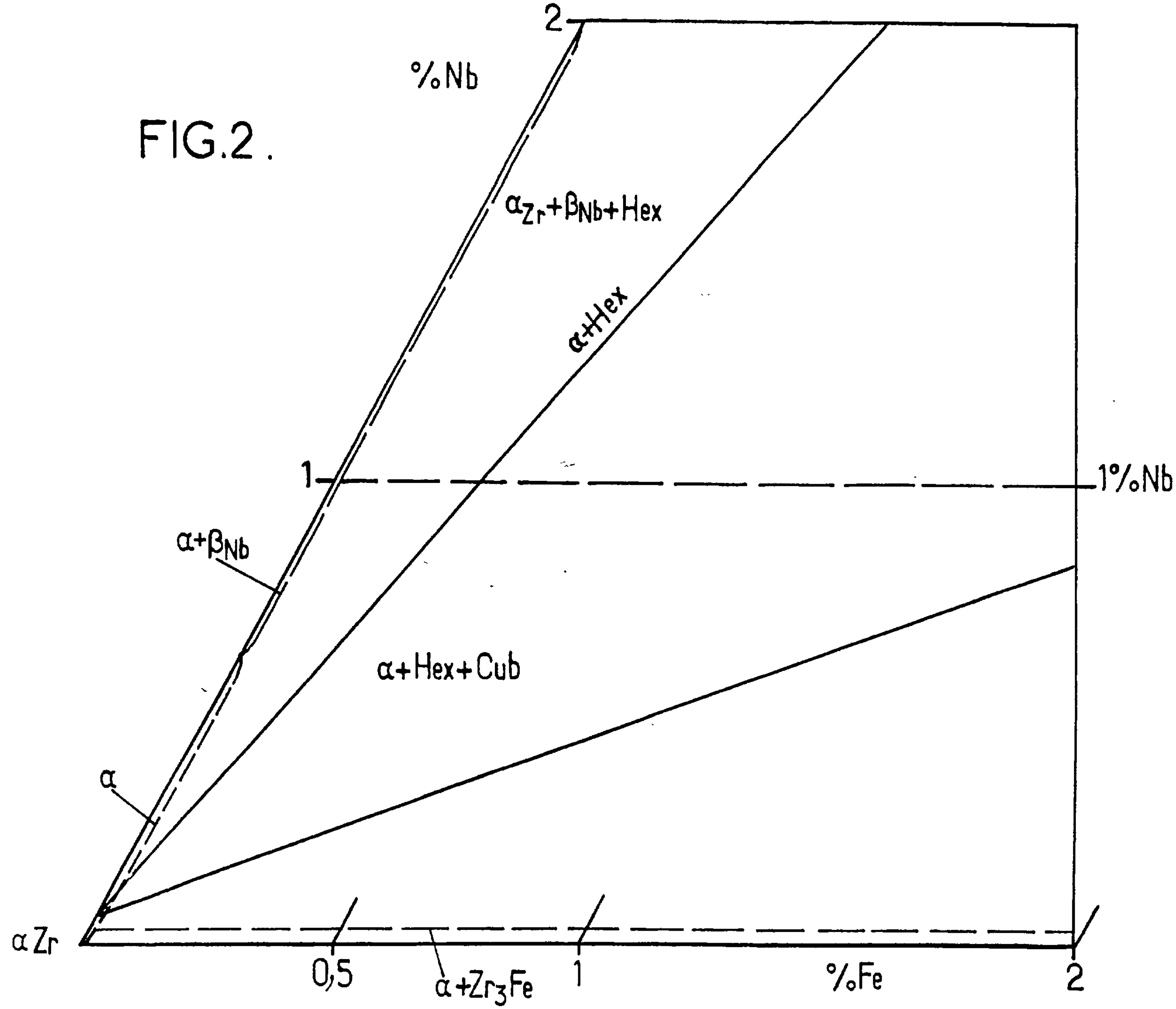
FIG.1.



Fe
%Fe
Nb
%Nb
β_{Nb}
$\alpha+\beta_{Nb}+Hex$
$\alpha+\beta_{Nb}$
$\alpha+Hex$
$\alpha+Hex+Cub$
Cub
$\alpha+Cub$
Zr_3Fe
Zr

FIG.2.



10/089481 JC13 Rec'd PCT/PTO

99010

U.S. DEPARTMENT OF COMMERCE
PATENT AND TRADEMARK OFFICE

DECLARATION AND POWER OF ATTORNEY

ATTORNEY'S DOCKET NO.

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled ______________________________, the specification of which

_____ is attached hereto.

__X__ was filed on September 28, 2000 as United States Application Number or PCT International Application Number PCT/FR00/02680 and was amended on ______________________ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

PRIOR FOREIGN APPLICATION(S)

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed:

COUNTRY	APPLICATION NUMBER	DATE OF FILING (day, month, year)	DATE OF ISSUE (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C § 119
FRANCE	99 12 248	September 30, 1999		Yes

NY01 420480 v 1

PRIOR UNITED STATES APPLICATION(S)

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

APPLICATION NUMBER	FILING DATE (day, month, year)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or §365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

APPLICATION NUMBER	FILING DATE (day, month, year)	STATUS (i.e. Patented, Pending, Abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorneys:

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I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

1-00

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Signature		Date APRIL 2, 2002	

2-00

FULL NAME OF INVENTOR	FAMILY NAME MARDON	FIRST GIVEN NAME Jean	SECOND GIVEN NAME Paul
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NY01 420480 v 1

3-00

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RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
Signature		Date	

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